

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in and relating to the Polymerisation of Olefines

- We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the polymerisation of olefines.
- In our co-pending British Application No. 37361/54 (Serial No. 785,314) it has been proposed to polymerise olefines by bringing the olefine into contact with a reaction medium comprising a solvent and a material formed by reacting an organo-compound of a non-transition metal of Groups 1, 2 or 3 of the Periodic System, such as an aluminium trialkyl, with a compound of a transition metal of Groups 4 to 6 of the Periodic System, such as titanium tetrachloride.
- The operation of processes of this type for the polymerisation of olefines in an economic manner depends in large measure on the cost of recovery of the solvent from the reaction product in a form suitable for re-use in the process. Processes for the recovery of a solvent by distillation usually involve high operating costs.
- We have now found that by the use of suitable low boiling solvent not only can a good yield of polymer be obtained but the solvent can be separated from the polymer in a highly economic way by vaporising the solvent, preferably by reducing the pressure. The solvent may then be reliquefied and returned to the process.
- According to the invention, therefore, there is provided a process for the polymerisation of olefines in which the olefine is brought into contact with a reaction medium comprising an inert solvent for the olefin, said solvent boiling below 40° C. at atmospheric pressure and a material formed by reacting at least one organo-compound of at least one non-transition metal as hereinafter defined of Groups 1, 2 and 3 of the Periodic System with a compound of a transition metal of Groups 4 to 6 of the Periodic System and in which the inert solvent is maintained in the liquid phase during the polymerisation reaction and is then vaporised, preferably by reduction of pressure, to separate it from the polymerised olefine.
- As a feature of the invention the vaporised liquid may be again liquified, preferably by cooling, and returned to the process. Alternatively the vapour may be liquified by compression and cooling.
- It is preferred to operate the process under conditions such that the solvent is under reflux during the polymerisation reaction. In this way there is provided a very convenient method of controlling the temperature at which the polymerisation reaction takes place.
- The solvent should boil below 40° C. and should be inert under the reaction conditions. Suitable solvents are paraffinic hydrocarbons containing up to 5 carbon atoms and olefines inert under the reaction conditions such as isobutylene. We prefer to use propane or butanes.
- The olefine may be a gas or a liquid under normal conditions of temperature and pressure. It should be brought into contact with the reaction medium so that it dissolves at least in part the solvent.
- Mixtures of olefines may be polymerised. The olefines may be pure or in admixture with substances, e.g. paraffinic hydrocarbons, which are inert under the conditions of the polymerisation reaction.
- The pressure at which the polymerisation is carried out should be at least sufficient to maintain the solvent in the liquid state. Higher pressures however may be used if desired.
- The temperature at which the polymerisation is carried out must not exceed the critical temperature of the solvent. Temperatures

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below 100° C. are particularly suitable. It is preferred to use temperatures within the range 60° to 70° C.

Water and oxygen should not be present in the apparatus in which the polymerisation is effected in more than relatively small amounts since they decompose organo-compounds. Air is suitably displaced from the apparatus by a gas inert under the reaction conditions, for example, nitrogen.

The invention is applicable to the polymerisation of ethylene and alpha-olefines. Examples of alpha-olefines are propylene, butene-1 and styrene.

The polymers produced by the process of the invention may be solid, high molecular weight polymers which are suitable for working up into, for example, filaments, foils, sheets and tubes having very desirable properties, or polymers of lower molecular weight which are suitable as chemical intermediates. The solid polymers may contain substantial amounts of material insoluble in ether and giving the regular X-ray diffraction pattern of a crystalline material.

A non-transition metal is defined as a metal of one of the short periods of the Periodic System or a metal of one of the long periods occupying one of the two places immediately following an inert gas or one of the seven places which immediately precede an inert gas. Examples of suitable non-transition metals are aluminium, beryllium, zinc, magnesium, lithium and sodium.

The organo-compound should contain at least one hydrocarbon radical attached to an atom of a non-transition metal, any remaining metal valencies being satisfied by hydrogen or halogen atoms.

Suitable hydrocarbon radicals include alkyl, alkenyl, alkynyl, cyclo-alkyl, aryl and aralkyl radicals, of which alkyl is preferred.

The organo-compound may be used in the form of a molecular compound with for example, ethers, thio-ethers or amines.

Mixtures of the above defined organo-compounds may be employed.

Particularly suitable organo-compounds are aluminium alkyls e.g. aluminium triethyl, or alkyl aluminium halides which may be produced by the processes of co-pending British Applications Nos. 1950/54 and 11773/54 (Serial No. 762,200). Other particularly suitable organo-compounds are complex alkyls of aluminium and an alkali metal such as $\text{LiAl}(\text{C}_2\text{H}_5)_4$, $\text{NaAl}(\text{C}_2\text{H}_5)_4$, which may be prepared by the process of co-pending British Application No. 31951/53 Serial No. 757,524. Suitable organo-compounds are alkali metal alkyls or aryls e.g. lithium butyl and sodium phenyl; zinc alkyls e.g. zinc dibutyl; alkyl hydrides of Group III metals e.g. aluminium ethyl dihydride, aluminium diethyl hydride and complex organo-compounds such as

$\text{NaAl}(\text{C}_2\text{H}_5)_4$, $\text{NaAl}(\text{C}_2\text{H}_5)_3\text{H}$, $\text{LiAl}(\text{C}_2\text{H}_5)_4\text{H}$, and $\text{KAl}(\text{CH}_3)_2\text{F}$. 65

The transition metal compound should be a compound of a transition metal of Groups 4 to 6 inclusive of the Periodic System. Suitable compounds are halides, oxyhalides, complex halides such as complex fluorides, alcoholates, acetates, benzoates and acetylacetonates of titanium, zirconium, hafnium, thorium, uranium, vanadium, niobium, tantalum, chromium, manganese, molybdenum and tungsten. Mixtures of transition metal compounds may be used. 70 75

We prefer that the transition metal compound is a halide such as, for example, titanium tetrachloride, titanium trichloride, vanadium tetrachloride, molybdenum pentachloride and tungsten hexachloride. 80

The organo-compound and the transition metal compound should preferably be brought together in a molecular ratio within the range 20:1 to 1:20. It is particularly convenient to use molecular ratios within the range 12:1 to 1:4. 85

A reaction medium containing the reaction products of small amounts of an organo-compound and a transition metal compound will effect the polymerisation of relatively large amounts of the olefin. However, in order to maintain a high conversion of the olefin into polymer it is desirable to add further quantities of organo-compound and transition metal compound to the reaction medium as required. 90 95

When the organo-compound contains only hydrocarbon radicals linked to a metal the catalytic activity of the reaction medium may be promoted by the presence of an organo-metal halide or a metal halide, particularly those halides which are catalysts for Friedel-Craft reactions. Very suitable promoters are alkyl aluminium sesquihalides, for example, ethyl aluminium sesquihalide. Another suitable promoter is aluminium chloride. Suitable amounts of the promoter are up to 20% by weight of the organo-compound. 100 105

EXAMPLE 1.

Ethylene was polymerised in an apparatus consisting essentially of a 1-litre flask fitted with a stirrer, a reflux condenser cooled by solid carbon dioxide and a gas inlet tube. Water was excluded from the apparatus and the air displaced by ethylene. 110 115

The reaction medium was prepared by introducing 0.035 moles aluminium triethyl and 0.035 moles titanium tetrachloride, each mixed with about 10 ml. of petroleum ether into the flask, vigorously stirring and then adding 400 ml. mixed liquid butanes. 120

With the temperature of the reaction medium about 0° C. and the butanes boiling steadily under reflux, dry ethylene gas was brought into contact with the reaction medium at the rate of 30 litres/hour. After 3 hours the flow of ethylene was stopped although the rate 125

of conversion of the ethylene showed no signs of decreasing. The reaction medium was then inactivated by the addition of alcohol and the butanes allowed to vaporize from the flask. The

- 5 butane vapour was condensed for re-use.
 34% of the ethylene used was converted into solid polyethylene, the total weight of polymer formed was 36 grams and the molecular ratio of ethylene polymerised to titanium tetrachloride used was 31:1.

EXAMPLE 2.

- Propylene was polymerised as described in Example 1 using 200 ml liquid butanes as the solvent. Propylene gas was brought into contact with the reaction medium for 0.5 hours at the rate of 30 litres/hour. 2.9 grams of solid polypropylene were obtained.

EXAMPLE 3.

- Two sealed glass phials containing 5.88 grams aluminium tripropyl and 5.50 grams titanium tetrachloride were placed in a 1 litre autoclave containing two steel balls for the purpose of breaking the phials on rocking the autoclave. The autoclave was then sealed, and the air in the autoclave displaced by nitrogen. 370 grams mixed butanes were then introduced into the autoclave followed by ethylene until the pressure reached 58 atmospheres. The autoclave was then rocked and heated at 60° C. After 30 minutes, when the pressure had fallen to 27 atmospheres further ethylene was introduced into the autoclave to restore the pressure to 58 atmospheres. After a further 5 hours the autoclave was cooled to room temperature and the pressure released to vaporise the butanes which were then condensed by cooling. After deactivating the reaction medium with alcohol 314 grams solid polyethylene was recovered from the autoclave.

- 40 We are aware of Patent No. 783,487 which claims "A process of polymerising ethylene to a solid polymer having a melt index within the range 0.005 to 3 which comprises continuously adding ethylene to a reaction zone wherein it is polymerised in an inert liquid hydrocarbon solvent at a temperature within the range 150° C. to 230° C. and under a pressure sufficient to maintain appreciable concentration of ethylene in the solvent, in the presence of a titanium containing complex as catalyst, said complex being produced by reducing a titanium compound in solution in an inert hydrocarbon solvent with an organometallic or metal hydride reducing agent, the ratio of titanium to reducing agent in the solution being from 0.4:1 to 1.4:1, whereby the valency of

the titanium in said complex is reduced to below 3, said polymerisation giving rise to a dissolved polymer which is continuously separated and removed from the reaction zone" in which the inert hydrocarbon solvent may be, *inter alia*, butane or pentane. We make no claim to anything claimed in Patent No. 783,487.

What we claim subject to the foregoing disclaimer is:—

1. A process for the polymerisation of olefines in which the olefine is brought into contact with a reaction medium comprising an inert solvent for the olefine, said solvent boiling below 40° C. at atmospheric pressure, and a material formed by reacting at least one organo-compound of at least one non-transition metal as hereinbefore defined of Groups 1, 2 and 3 of the Periodic System with a compound of a transition metal of Groups 4 to 6 of the Periodic System and in which the inert solvent is maintained in the liquid phase during the polymerisation reaction and is then vaporised, preferably by reduction of pressure, to separate it from the polymerised olefine.

2. A process as claimed in Claim 1 in which the inert solvent is under reflux during the polymerisation reaction.

3. A process as claimed in Claims 1 or 2 in which the vaporised inert solvent is liquefied again by cooling and returned to the process.

4. A process as claimed in any of the previous claims in which the inert solvent is propane or butanes.

5. A process as claimed in any of the previous claims in which the temperature is below 100° C.

6. A process as claimed in any of the previous claims in which the temperature is within the range 60° to 70° C.

7. A process as claimed in any of the previous claims in which the organo-compound is an aluminium alkyl.

8. A process as claimed in any of the previous claims in which the transition metal compound is a halide.

9. A process as claimed in any of the previous claims in which the transition metal compound is titanium tetrachloride.

10. A process for the polymerisation of olefines whenever carried out as described in any of the foregoing examples.

11. Olefine polymers whenever produced by a process as claimed in any of the preceding claims.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improvements in and relating to the Polymerisation of Olefines

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare this invention to be described

5 in the following statement:—

This invention relates to the polymerisation of olefins.

The term "olefin" is to be taken to include aliphatic olefins and aromatic olefins, for example, styrene. The term "polymerisation" is to be taken to include dimerisation.

10 It is an object of the invention to provide a process whereby olefins are polymerised smoothly and rapidly to polymers, those of higher molecular weight being eminently suitable for working up into, for example, filaments, foils, sheets and tubes having very desirable properties, and those of lower molecular weight being eminently suitable as chemical intermediates.

20 According to the invention there is provided a process for the polymerisation of olefins in which the olefin in the liquid phase is brought into contact with a reaction medium comprising a material formed by reacting an organo-metal compound with a metal compound both as hereinafter defined.

The organo-metal compound should be a compound of a non-transition metal i.e. a metal of one of the short periods of the Periodic System or a metal of one of the long periods occupying one of the two places immediately following an inert gas or one of the seven places which immediately precede an inert gas. Examples of suitable non-transition metals are aluminium, boron, beryllium, zinc, magnesium, lithium and sodium.

30 When the non-transition metal is an alkali metal the organo-metal compound should then contain a saturated or unsaturated hydrocarbon radical.

45 When the non-transition metal is not an alkali metal the organo-metal compound should be one in which the metal is combined with saturated hydrocarbon radicals, unsaturated hydrocarbon radicals or hydrogen atoms in any combination or a compound in which the metal is combined with halogen atoms and at least one saturated or unsaturated hydrocarbon radical. Suitable hydrocarbon radicals include alkyl, alkenyl, alkynyl, cyclo-alkyl, aryl and aralkyl radicals.

50 Mixtures of the above defined organo-metal compounds may be employed. The organo-metal compound may also be used in the form of a complex compound with an alkali metal hydride, alkyl or aryl or in the form of a molecular compound with, for example, ethers, thioethers or amines. Particularly suitable organo-metal compounds are aluminium alkyls or alkyl aluminium halides which may be produced by the processes of co-pending Applications Nos.

1950/54 and 11773/54. Other very suitable organo-metal compounds are complex alkyls e.g. sodium aluminium tetra-ethyl, lithium aluminium tetra-propyl; alkali metal alkyls or aryls e.g. lithium propyl and sodium phenyl; zinc alkyls e.g. zinc di-ethyl and hydrides of Group III metals e.g. aluminium hydride, aluminium ethyl dihydride, aluminium diethyl hydride, gallium hydride.

70 The metal compound should be a compound of a transition metal of Groups IV to VIII inclusive of the Periodic System. Suitable compounds are halides, oxyhalides, complex halides such as complex fluorides, freshly precipitated oxides or hydroxides, alcoholates, acetates, benzoates and acetylacetonates of titanium, zirconium, hafnium, thorium, uranium, vanadium, niobium, tantalum, chromium, manganese, molybdenum and tungsten. Mixtures of the above defined metal compounds may be used and these mixtures may be used with mixtures of the organo-metal compounds. We prefer to use a halide such as for example vanadium tetrachloride, molybdenum pentachloride, tungsten hexachloride and manganic chloride. A particularly suitable halide is titanium tetrachloride.

85 The organo-metal compound and the metal compound may be brought together in a wide range of molecular ratios. The choice of a particular ratio depends on the properties, particularly the physical properties, required in the polymer. While the effect of other factors e.g. pressure, temperature, composition of the organo-metal compound, must be taken into account, in general increase in the molecular ratio organo-metal compound/metal compound leads to a decrease in the viscosity and molecular weight of the polymer. Thus, by suitable choice of the molecular ratio dimers and a wide range of polymers from liquid polymers to solid polymers of high viscosity may be produced.

100 The molecular ratio organo-metal compound/metal compound also affects the yield of polymer. In general, increase in the ratio leads to an increase in the conversion of olefine into polymer.

110 It is preferred that the molecular ratio organo-metal compound/metal compound should be within the range 20:1 to 1:20. Suitable ratios are 15:1, 10:1, 8:1, 6:1, 4:1 and less. In producing solid polymers of high viscosity it is preferred to use molecular ratios within the range 4:1 to 1:4, particularly a ratio of 1:1, in order to use valuable metal compound economically. Lower ratios than 1:4 may however be used, suitably 1:6, 1:8, 1:10 and 1:12.

120 The catalytic activity of the medium is promoted by the presence of an organo-metal halide or a metal halide, particularly those halides which are catalysts for Friedel-Craft

reactions. Very suitable promoters are alkyl aluminium sesquihalides, for example, ethyl aluminium sesquichloride. Another suitable promoter is aluminium chloride. The amount of promoter used may vary over a wide range. For example, up to 20% of the weight of the organo-metal compound may be used though it is preferred to use up to 10% while a very suitable amount is 1% by weight.

As well as affecting the catalytic activity of the medium the above described promoters affect the viscosity of the polymer produced. Thus for a given molecular ratio of organo-metal compound to metal compound the polymer formed may have a higher viscosity in the presence than in the absence of a promoter. The polymerisation process may be carried out using a promoted reaction medium in which the organo-metal compound and metal compound are brought together in any of the molecular ratios hereinbefore described.

The reaction medium preferably comprises a solvent which may be the olefin it is desired to polymerise. Except when the solvent is an olefin taking part in the polymerisation process, the solvent should be substantially inert under the reaction conditions. Suitable inert solvents are paraffinic, aromatic and alicyclic hydrocarbons. Normally gaseous substances may be used as solvents provided that they are liquid under the conditions of temperature and pressure employed in the polymerisation process. Suitable solvents are butanes, pentanes, hexanes, cyclohexane, methyl cyclohexane and toluene.

Mixtures of olefins may be polymerised. The olefins may be pure or in admixture with substances e.g. other hydrocarbons, which are inert under the conditions of the polymerisation reaction.

The polymerisation process may be carried out at temperatures within a wide range provided that the temperature does not exceed

the critical temperature of the olefin. For example, temperatures up to 300° C. or higher may be used. It is preferred however to employ temperatures below 60° C. say 40° C. Very suitable temperatures are within the range 0° to 20° C. Lower temperatures than 0° C. may however be used.

The pressure at which the polymerisation is carried out may be atmospheric or higher or lower pressures. The pressure however, should be sufficient to maintain the olefin in the liquid phase.

It is preferred to operate the polymerisation process under such conditions of pressure and temperature that the reaction mixture is under reflux. Operation under reflux conditions provides a very convenient method of controlling the temperature of the reaction mixture and thereby the properties of the product. The composition of the reflux depends on the relative vapour pressures of the solvent if used and the olefin; it may consist mainly of olefin or mainly of solvent. In conjunction with the reflux process it is preferred to use a low boiling solvent for example, ethane, propane, butanes and pentanes. By so doing the solvent may be easily separated from the polymer and returned to the reaction zone. It is preferred to separate the solvent from the polymer by a suitable reduction of pressure and then to re-liquify the solvent vapour by compression. The reflux process is particularly applicable to the polymerisation of, for example, ethylene, propylene, butene-1 and isobutylene. The process may be operated in a continuous manner.

Water and air must be excluded from the apparatus in which the polymerisation is effected. Air is suitably displaced from the apparatus by an inert atmosphere of, for example, nitrogen.

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